

Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 5-2. Basic Operations that may be used in the Production of Styrene by Ethylbenzene Dehydrogenation

Source: References 14 and 74.

The hydrogen-rich process gas is recovered and used as a fuel (Stream 7) and the process water is purified in a stripper and recycled to the boiler. The remaining crude styrene liquid (Stream 6) goes to a storage tank. Benzene and toluene (Stream 8) are removed from the crude styrene in the benzene/toluene column. They are then typically separated by distillation. The toluene is sold and the benzene is returned to ethylbenzene production section (Stream 10), or it may also be sold. Next, the ethylbenzene column removes ethylbenzene, which is directly recycled (Stream 1). Tars are removed and the product styrene (Stream 9) emerges from the styrene finishing column. In some facilities, an ethylbenzene/benzene/toluene stream is separated from the crude styrene initially and then processed separately.

Emission points in this process include vents from the columns for the styrene purification section between the separator and the recovery sections. These include the benzene toluene column (Vent A), the ethylbenzene recycle column (Vent B) and the emergency vent in the styrene finishing column (Vent C). Other emission points from the process including storage tanks and barge loading are shown in Figure 5-2.

#### 5.1.2 Process Description for Ethylbenzene Production from Mixed Xylenes

Ethylbenzene can also be extracted from mixed xylene streams. Proportionately, however, very little ethylbenzene is produced in this fashion. The two major sources of ethylbenzene containing xylenes are catalytic reformat from refineries, and pyrolysis gasoline from ethylene production (see process description for ethylene production in Section 4.3). The amount of ethylbenzene available is dependent on upstream production variables. The ethylene separation occurs downstream of the benzene production. For this reason, the ethylbenzene produced by this process is not considered a source of benzene emissions. Instead, benzene emissions from the entire process train are considered to be emissions from benzene production and are included elsewhere in this document (Section 4.0).

When combined with the dehydrogenation process previously described to produce styrene (Figure 5-2), the process is similar except that the benzene recycling (Stream 10 in Figure 5-2) cannot be reused directly.

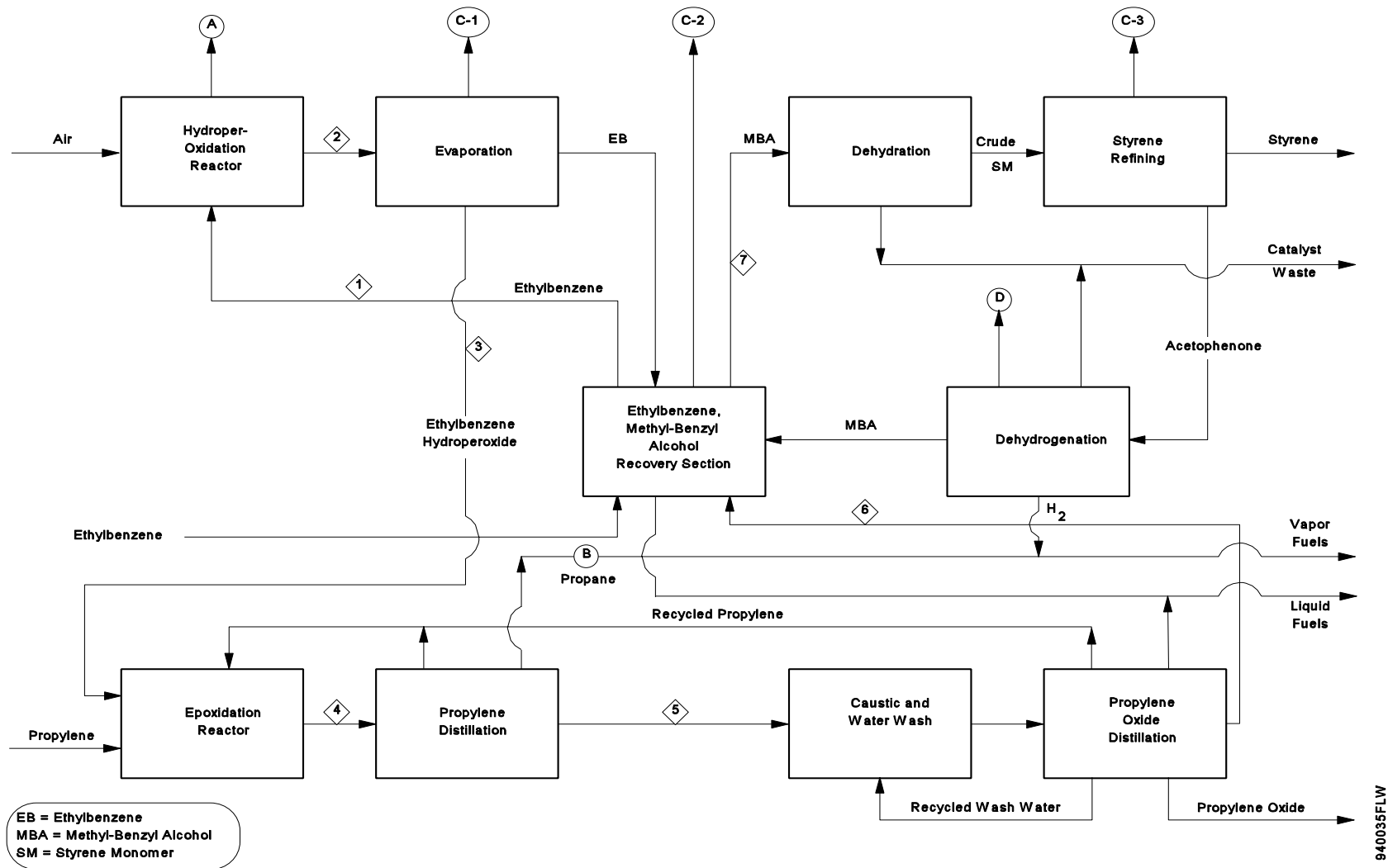
#### 5.1.3 Process Description for Styrene Production from Ethylbenzene Hydroperoxidation

Presently, only one U.S. facility uses the hydroperoxidation process to produce styrene. Figure 5-3 shows a process flow diagram. The four major steps are described below.

Ethylbenzene (Stream 1) is oxidized with air to produce ethylene hydroperoxide (Stream 2) and small amounts of  $\alpha$ -methyl-benzyl alcohol and acetophenone. The exit gas (principally nitrogen) is cooled and scrubbed to recover aromatics before venting. Unreacted ethylbenzene and low-boiling contaminants are removed in an evaporator. Ethylbenzene is then sent to the recovery section to be treated before reuse.

Ethylbenzene hydroperoxide (Stream 3) is combined with propylene over a catalyst mixture and high pressures to produce propylene oxide and acetophenone. Pressure is then reduced and residual propylene and other low-boiling compounds (Stream 4) are separated by distillation. The vent stream containing propane and some propylene can be used as a fuel. Propylene is recycled to the epoxidation reactor. The crude epoxidate (Stream 5) is treated to remove acidic impurities and residual catalyst material and the resultant epoxidate stream is distilled to separate the propylene oxide product for storage.

Residual water and propylene are recycled to the process train and liquid distillate is recovered as a fuel. The organic layer is routed (Stream 6) to the ethylbenzene and  $\alpha$ -methyl-benzyl alcohol recovery section. Distillation removes any remaining ethylbenzene. Organic waste streams are separated from the  $\alpha$ -methyl-benzyl alcohol and acetophenone organic waste liquids are used as fuel.



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Figure 5-3. Ethylbenzene Hydroperoxidation Process Block Diagram

Source: Reference 74.